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REFRACTORY MATERIALS AS A FIELD FOR RESEARCH

By Edward W. Washburn

Chairman, Committee on Ceramic Chemistry, National Research Council

Published in the *Journal of the American Ceramic Society*
January, 1919, vol. 2, no. 1, pages 3–31

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REPRINT AND CIRCULAR SERIES

OF THE

NATIONAL RESEARCH COUNCIL

NUMBER 3

REFRACTORY MATERIALS AS A FIELD FOR RESEARCH

A SURVEY OF THE SCIENTIFIC ASPECTS OF THE SUBJECT*

By Edward W. Washburn

Chairman, Committee on Ceramic Chemistry, National Research Council

1. Definition of the term refractory material.—For the purpose of defining an homogeneous class of materials for systematic investigation, the term 'refractory material' *will be here understood* to signify any non-metallic material capable of withstanding elevated temperatures, without destruction or deterioration (by fusion, sublimation, chemical decomposition or physico-chemical transformations) so rapidly as to preclude its use in the construction of vessels, linings, furnace walls, flues, etc., subjected to high temperatures. Although resistance to high temperatures is the primary and distinguishing characteristic demanded of refractory materials as a class, almost every refractory employed in modern industry must also exhibit, while at a high temperature, an adequate resistance toward one or more of the following destructive agents: (1) pressure or load; (2) mechanical vibration; (3) frequent, rapid and unequal heating or cooling, or any one or more of these; (4) the stresses set up by expansion or contraction of other parts of the furnace or vessel of which the refractory material is a component part; (5) mechanical abrasion by ashes, cinders, etc., or by the furnace charge itself; (6) the chemical action of atmospheric and furnace gases; (7) the slagging action of the furnace charge or of materials given off by it; and (8) the chemical

* Reprinted from the *Journal of the American Ceramic Society*, January, 1919, 2, no. 1, p. 3–31.

This report was drafted under the auspices of the Section of Industrial Research of the National Research Council, as a preliminary step in the consideration of the nature of the problems involved in research in this field and of the possibilities of attacking them by concerted action.

action of any other furnace parts such, for example, as the electrodes or the heating element in an electric furnace; and in certain special cases the refractory must (9) while at high temperature (*a*) remain a good electrical insulator, or (*b*) become an electrical conductor; or (10) (*a*) remain a good thermal insulator, or (*b*) become to a given degree a thermal conductor.

2. The importance of the subject.[1]—Every industrial plant which employs high temperatures in any part of its work has a more or less acute problem of refractory materials to deal with. The refractory materials employed may vary in type all the way from the ordinary firebricks (such as are employed in the boiler settings of the power plant) up to highly specialized materials designed to withstand one or more of the special destructive agents mentioned above. Railway locomotives and the power plants of ships can be operated with the highest efficiency only when properly designed refractory materials are used in their construction. Practically all of the metallurgical industries, both those which have to do with the extraction of metals from ores as well as those engaged in working the various metals or preparing alloys, have especially trying and difficult refractory problems to meet. An important part is also played by refractory materials in the manufacture of electric furnace products (such as abrasive materials, graphite, carbide, nitrogen products from the air, and a variety of other chemical products); of glass and quartz articles; of lime, cement, potash, fuel gas, ammonia, coke, and many of the pigments; and of course of all ceramic products.

As a field for industrial research, the subject of refractory materials is, therefore, fundamental in character, widespread in its practical applications and of great national importance. The present trend of many industries in the direction of using increasingly high temperatures[2] in their operations is a further indication of the growing importance of a thorough and systematic scientific investigation of the various problems connected with the preparation and use of refractory materials.

3. Conservation of fuel.—In a high temperature furnace or kiln, where the internal temperature required is higher than the refractory lining will withstand, it is customary to protect this lining by artificial cooling either by means of air or water. Such artificial cooling naturally results in a great waste of heat and in a corresponding greater consumption of fuel. The ideal arrangement would be to cover the outside of the furnace with a good thermal insulator so as to retain this heat in the furnace, but in many cases under present conditions such an insulation would result in the rapid destruction of the refractory lining, owing to the fact that this lining would soon attain the temperature of the inside of the

furnace. It is obvious that the development of refractory materials which would permit the thermal insulation of industrial furnaces would result in an enormous fuel saving since the wastage resulting from present methods is one of the large elements in the total fuel consumption of industrial furnaces. Perfect adaptation of the refractory to furnace conditions (temperature, pressure, chemical action, mechanical abrasion, etc.) is one of the big problems whose successful solution would constitute a great contribution to the fuel conservation movement.

4. *Annual production and consumption of refractory materials in the United States.*—Complete statistics on the annual production of refractory materials and products in the United States do not seem to be available in public records but from the data at hand the value of the annual production of such materials may be safely estimated as greater than sixty million dollars.

The following statistical data on the subject have been recently compiled at the writer's request from the records of the United States Geological Survey.

Bauxite refractories.—In 1917 the bauxite used for the manufacture of refractory wares was about 12,000 tons. Approximately three million bricks $2\frac{1}{2}$ x $4\frac{1}{2}$ x 9 inches were sold, valued from \$50 to \$380 per thousand. In 1917 the bauxite used in the manufacture of refractory wares was over 2500 tons, but exact figures are not available, nor is information as to the quantity or value of the products made.

Refractories manufactured from quartz, chert, silica, fused silica, etc.—Except as elsewhere noted concerning silica brick, the Geological Survey has no record of the manufacture or production statistics of refractory wares made of these materials. Only the total output of silica in various raw forms is known, and this is not separated or classified according to uses.

Refractories manufactured from ganister.—There is no available record of the refractory wares and materials made of ganister. The Survey's record of ganister production—that is, sales of quarry products—is as follows:

Production 1913–1917

YEAR	SHORT TONS	VALUE
1913		\$ 376,775
1914		288,244
1915	573,304	336,267
1916	859,956	529,805
1917	1,001,630	1,117,558

Mica schist for furnace lining.—The following data concerning the production of mica schist for furnace linings are available:

Production 1913–1917

YEAR	SHORT TONS	VALUE
1913		$45,102
1914		54,567
1915		24,625
1916	33,236	47,304
1917	39,975	85,986

Magnesite refractories.—Statistics of the quantity and value of magnesite produced and sold in the United States are available, but no information is at hand as to the proportions of this material which enter into refractories, magnesium chloride, magnesia-alba, manufacture of paper and other products. The Geological Survey assumes that the only source of information as to the quantity of refractory brick and shapes made from magnesite in the United States would be by a canvass of the manufacturers.

Dolomite refractories.—The Geological Survey has only the following statistical information:

Estimate of dolomite and equivalent in 'dead burned' lime, produced for refractory purposes 1914–1917

YEAR	DEAD BURNED, SHORT TONS	UNBURNED, SHORT TONS
1914	13,053	26,058
1915	50,223	100,446
1916	136,240	267,446
1917	176,876	234,720

Chromite refractories.—There is no available information on the quantity and value of chromite used in the manufacture of refractory wares, or on the value of the refractories manufactured, other than statistical data showing that 4364 long tons of chromite in the form of refractories were consumed during the first half of 1918 and that 1959 long tons were similarly consumed during July, 1918.

Graphite refractories.—So far as known to the United States Geological Survey, there are no statistics showing quantity of molded graphite articles, such as graphite crucibles, anywhere available for the years asked for, or for that matter, for any periods.

Quartz-glass and fused silica refractories.—No available data.

Zirconia refractories.—Data concerning the total annual production of zirconium minerals are contained in the Annual Mineral Resources Reports.

Rare earth refractories.—The following information is taken from the report on the gas-mantle industry now in the files of the United States Tariff Commission.

Production and importation of thorium nitrate in the United States, 1913–1917

YEAR	QUANTITY PRODUCED	QUANTITY IMPORTED
	pounds	*pounds*
1913	Information confidential cannot be published	112,105
1914		144,413
1915		78,516
1916		22,261
1917		1,877

Clay refractories.—The following statistics on the value of clay refractories manufactured in the United States for the years 1913 to 1916 have been compiled by the United States Geological Survey:

PRODUCT	1913	1914	1915	1916
Fire brick, including refractory block or tile, boiler and locomotive tile, tank blocks and similar refractory products	$16,811,316	$13,476,022	$15,800,062	$25,155,519
Other fire brick, including some special shapes, etc.	134,635	115,144	121,747	311,052
Silica brick, including clay-bond and lime-bond brick	3,815,806	2,951,525	3,039,869	5,650,610
Zinc retorts	(*c*)	576,655	823,545	1,553,691
Zinc condensers	(*d*)	176,591	260,436	512,453
Glass melting pots and other glass-house refractories (Special effort to collect statistics of these products from the consumer manufacturing for his own use was not made prior to 1915)	568,603	498,096	719,889	1,989,754
Gas retorts	65,846	41,372	23,835	35,821
Charcoal furnaces (portable)	37,217	36,243	32,865	27,280
Muffles, scorifiers, assay supplies and crucibles (other crucibles are included with chemical porcelain and chemical stoneware)	63,869	67,367	98,105	364,563
Saggers (prior to 1917 statistics for saggers were not collected from the sagger consumer manufacturing for his own use)	(*e*)	(*e*)	(*e*)	34,476

PRODUCT	1913	1914	1915	1916
Chemical porcelain and chemical stoneware	(*f*) 224,894	(*f*) 246,918	(*f*) 620,401	1,054,061
Potters' supplies (pins, stilts, and spurs)	125,987	130,740	126,780	188,643
Mantle rings and special ware for gas lighting and heating, including magnesia ware and refractory porcelain for electric ranges and heaters (including a small valuation for pins and stilts)	(*e*)	(*e*)	172,261	220,849
Undistributed refractory products	364,519	329,423	22,288	
Total	$22,212,692	$18,646,096	$21,862,083	$37,098,772

(*c*) Reported by one producer only for 1913, and included with 'Undistributed refractory products'—statistics for zinc retorts were not collected prior to 1914.

(*d*) Reported by one producer only for 1913 and included under Miscellaneous—statistics for zinc condensers were not collected prior to 1914.

(*e*) Reported by less than three producers—included in 'Undistributed refractory products.'

(*f*) Chemical porcelain and chemical stoneware, not separately classified prior to 1916, were probably partly reported under Stoneware and *Yellow* and Rockingham ware in 1913, 1914, and 1915.

5. *An organization for the prosecution of research in refractory materials.*—In outlining and describing the various aspects of the subject of refractory materials as a field for research, we shall first create, for convenience of presentation, an hypothetical organization, which we shall assume proposes to engage in a complete and systematic study of *all problems* connected with the nature, preparation, properties, and industrial application of refractory materials. It should be understood that the particular organization described below is a purely fictitious one created on paper, merely as a convenient machine for setting forth in systematic fashion the various scientific aspects presented by the subject of refractory materials as a field for research. It is not suggested that this type of organization would be the most suitable one for actually undertaking to carry out research in this field, since in constructing an actual working organization various practical questions would have to be considered which do not enter into a plan of organization designed merely to display the different scientific aspects of the problem. It is not the writer's intention to propose at this time any particular type of working organization since the formation of such an organization would require the combined labors of a group of experts familiar with all of the practical questions involved. It is hoped, however, that the type of organization

employed here, for the purpose indicated, will, in so far as it sets forth in systematic manner all of the various scientific aspects of the subject, be convenient as a starting point in planning some practical working organization for undertaking the solution of the many important questions which our subject presents.

With this explanation therefore we shall assume that our hypothetical research association or corporation finds it convenient to organize itself into divisions for handling the different parts of its work. These divisions might be somewhat as follows.

A. The Board of Trustees and the Executive Committee.

B. The Scientific Director and the Advisory Committee.

(1) The Division of Statistics, Publication and Indexing.

(2) The Division of Phase-Rule Investigations.

(3) The Division of Physical, Chemical, and Ceramic Properties of Raw Materials and Manufactured Products.

(4) The Division of Standard Methods for Testing Refractory Products.

(5) The Division of Raw Materials Specifications.

(6) The Division of Manufacturing Methods.

(7) The Division of Standard Specifications for Refractory Products.

(8) The Engineering Division.

(9) The Division of Geology and Mining.

(10) The Division of Coördination and International Coöperation.

6. The Board of Trustees and the Executive Committee.—The Board of Trustees would be charged with the raising and expenditure of all funds and would exercise general supervision over the financial affairs of the Association. It would elect the Scientific Director and on his nomination appoint the chiefs of all Divisions.

The Executive Committee of the Board would be empowered to act for the Board in the intervals between Board meetings. After receiving the recommendations of the Advisory Committee, it would prepare the annual budget for presentation to the Board of Trustees and would also prepare the program of business for each meeting of the Board.

7. The Scientific Director and the Advisory Committee.—The Scientific Director would exercise general supervision over all of the research work of the Association. He would make all nominations for heads of Divisions and would transmit to the Executive Committee, with his recommendations, all nominations for appointment to positions on the research staff. For a time at least, he might also act as the head of one of the Divisions since he would presumably be specially qualified as an expert in at least one of the principal lines of work of the Association.

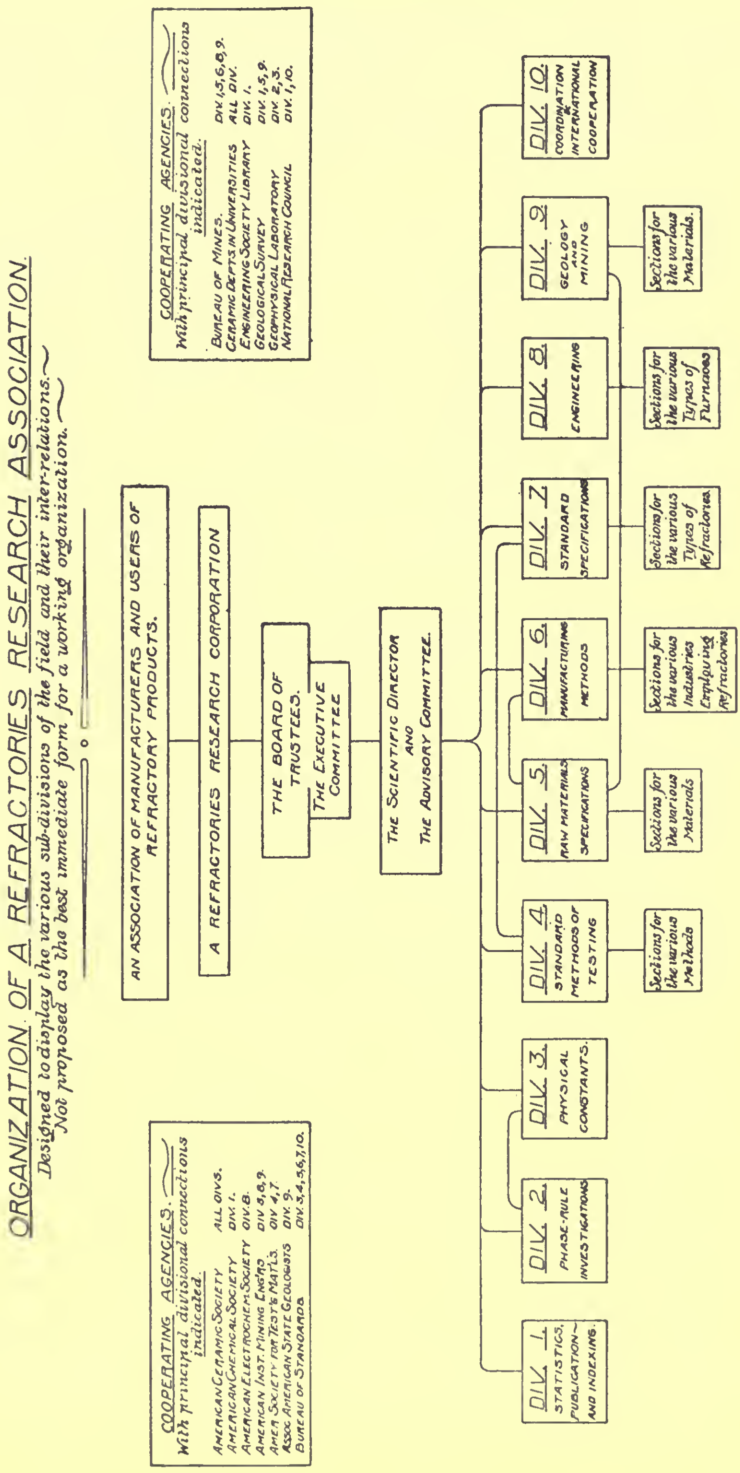
ORGANIZATION OF A REFRACTORIES RESEARCH ASSOCIATION.
Designed to display the various sub-divisions of the field and their inter-relations.
Not proposed as the best immediate form for a working organization.
COOPERATING AGENCIES. With principal divisional connections indicated.
AMERICAN CERAMIC SOCIETY ALL DIVS.
AMERICAN CHEMICAL SOCIETY DIV. 1.
AMERICAN ELECTROCHEM. SOCIETY DIV. 8.
AMERICAN INST. MINING ENG'RS. DIV 5,8,9.
AMER. SOCIETY FOR TEST'G MAT'LS. DIV 4,7.
ASSOC. AMERICAN STATE GEOLOGISTS DIV. 9.
BUREAU OF STANDARDS DIV. 3,4,5,6,7,10.
COOPERATING AGENCIES. With principal divisional connections indicated.
BUREAU OF MINES. DIV. 1,5,6,8,9.
CERAMIC DEPTS. IN UNIVERSITIES ALL DIV.
ENGINEERING SOCIETY LIBRARY DIV. 1.
GEOLOGICAL SURVEY DIV. 1,5,9.
GEOPHYSICAL LABORATORY DIV. 2,3.
NATIONAL RESEARCH COUNCIL DIV. 1,10.
AN ASSOCIATION OF MANUFACTURERS AND USERS OF REFRACTORY PRODUCTS.
A REFRACTORIES RESEARCH CORPORATION
THE BOARD OF TRUSTEES.
THE EXECUTIVE COMMITTEE
THE SCIENTIFIC DIRECTOR AND THE ADVISORY COMMITTEE.
DIV. 1. STATISTICS, PUBLICATION AND INDEXING.
DIV. 2. PHASE-RULE INVESTIGATIONS
DIV. 3. PHYSICAL CONSTANTS.
DIV. 4. STANDARD METHODS OF TESTING
DIV. 5. RAW MATERIALS SPECIFICATIONS
DIV. 6. MANUFACTURING METHODS
DIV. 7. STANDARD SPECIFICATIONS
DIV. 8. ENGINEERING
DIV. 9. GEOLOGY AND MINING
DIV. 10. COORDINATION & INTERNATIONAL COOPERATION
Sections for the various Methods
Sections for the various Materials
Sections for the various Industries Employing Refractories
Sections for the various Types of Refractories
Sections for the various Types of Furnaces
Sections for the various Materials.

FIG. 1.

The chiefs of all Divisions, together with possibly one or two additional members of national reputation as experts in industrial research, would constitute an Advisory Committee to the Scientific Director. This Committee would be charged with the preparation of the annual program of research and the necessary budget for accomplishing it. This program and budget would be transmitted by the Director to the Executive Committee of the Board of Trustees, which body would exercise the final judgment concerning the program and budget to be presented to the Board.

8. Division 1. Statistics, publication and indexing.—The duties of this Division would be as follows:

(1) The preparation of an exhaustive classified bibliography of the extensive and widely scattered literature on the subject of refractory materials and all matters relating thereto. This bibliography should be indexed and cross-indexed to the fullest degree so that the literature might be utilized to the best possible advantage. After publication this bibliography should be kept up to date by means of annual or semi-annual supplements which might be combined decennially into new editions.

(2) By coöperation with the American Chemical Society, the work of securing and publishing abstracts of all papers dealing with any aspect of the subject of refractory materials should be promoted and improvements secured in the abstracting and in the arrangement and cross-indexing of the abstracts in the pages of *Chemical Abstracts.*

(3) To supplement the above bibliographic material, the Division might arrange with competent experts for the preparation and publication, from time to time, of critical digests in the form of monographs on selected topics. Each of these monographs should be an exhaustive, critical presentation and discussion of all the essential known facts concerning the subject matter and should contain a complete set of tables of numerical data and a complete bibliography. In this way, it would be possible to build up gradually a library of authoritative and trustworthy works of reference dealing with all the various aspects of refractory materials and their uses.

Each important refractory material (silica, magnesite, kaolin, alumina, etc.) might become the subject of such a monograph as might also the practice and requirements of each type of industry employing refractories. Not the least value of such a set of monographs would be its revelation of the relatively small amount of really reliable scientific data available on the subject of certain refractories and the enormous amount of

work which still remains to be accomplished. The preparation of such a monograph should precede the undertaking, on any extensive scale, of a program of research on any given topic.

(4) The biennial publication of a handbook of tables of physical, chemical and ceramic constants relating to refractory materials and products as well as standard methods for testing and examination would be valuable. In the preparation of such a handbook, this Division would work in coöperation with Division 3.

(5) Either through the medium of a journal of its own, or preferably through arrangements with one or more established journals, the Division should provide for the publication of all investigations carried out under the auspices of the Association, in all cases where such publication has been approved by the Board of Trustees.

(6) By coöperation with the appropriate governmental agencies, such as the Bureau of the Census and the United States Geological Survey, the Division should endeavor to secure improvements in the collection of statistics relating to refractory raw materials and manufactured products, to the end that all valuable statistical information on this subject may be properly collected and classified.

(7) This Division might also become responsible for the more general diffusion of accurate information concerning the manufacture and use of refractory materials and to this end might inaugurate a publicity program for educational purposes.

9. Division 2. Phase-rule investigations.—This Division would have general charge of the initiation, promotion, and direction of the most fundamental as well as the most difficult and expensive scientific studies which are required in building up our scientific knowledge of refractory materials as chemical substances.

As regards the common characteristic possessed by all refractory materials, that of resistance to high temperature, the initial problem presented for experimental investigation is to a large degree a problem in physical chemistry involving as its most important feature the application of the phase-rule and the laws of solutions. Thus, in accordance with the known laws of physical chemistry, the effect of the presence of impurities in a refractory material is always to decrease the refractory power,[3] except when the proportion of the impurity is so large as to cause the composition of the mixture to coincide with a maximum point in the phase-rule diagram for the system, under which conditions the effect of the 'impurity' may be either a decrease, an increase, or no change at all in the refractory power, depending upon the materials involved. Ac-

cording to the same laws, it is also in nearly all cases true that the larger the number of materials employed in the manufacture of a refractory product, the lower will be its refractory power. A great many of the patents issued for refractory materials cover products whose manufacture violates all of the principles mentioned above. These principles are also violated in the rather widespread idea that, as a general rule, the refractory power of a given material can be increased by mixing with it a second, *more refractory material.* Indeed the various formulas, which are given in text books and treatises on ceramic subjects, for calculating the refractory power (i.e., softening point) of a mixture from its composition and the melting points of its components, seem to have been formulated without regard to established physico-chemical laws.

An illustrative example.—In order to illustrate the importance and the fundamental character of the physico-chemical relations displayed by the phase-rule diagram, in the solution of problems connected with the manufacture and use of refractories, a brief consideration of such a diagram for the system magnesia-alumina, will be given here. In other words, given the two substances magnesia, MgO and alumina, Al_2O_3, what are the possibilities, as displayed by the phase-rule diagram, of manufacturing refractory products from these two materials? The phase-rule diagram for this system is shown in figure 2.[4] In this figure temperatures are indicated vertically and compositions, expressed in weight percent, horizontally.

Both magnesia and alumina are separately employed in the industries as refractory materials. Alumina, however, at present market prices is considerably cheaper per pound than magnesia. Either substance when employed alone presents the difficulty of finding a suitable bonding material to use when shaping into the desired form, since any foreign bonding material which remains in the product after firing results in a lowering of the refractory power, while a bonding material which burns out during the firing leaves a loose structure with insufficient mechanical strength for many purposes.

The diagram shows that pure magnesia will not liquefy until a temperature of 2800°C. is attained. In other words, as far as its mere resistance toward softening at high temperatures is concerned, magnesia is one of the most refractory substances which we have. Although no liquefaction occurs below 2800°C. considerable deterioration occurs at much lower temperatures owing to crumbling, spalling, and sublimation, the volatility of the magnesia being so high that at high temperatures the magnesia vapors from a furnace lining will fill the whole interior of the

furnace and condense upon everything contained therein. This characteristic makes it undesirable to use magnesia as a refractory for many purposes.

In order to increase the mechanical strength of a refractory body, both in the green state and after firing, it is frequently customary to mix with the principal constituent a small amount of a second constituent to act as a bond. For example, let us suppose that small amounts of alumina were mixed with magnesia for this purpose. The problem then

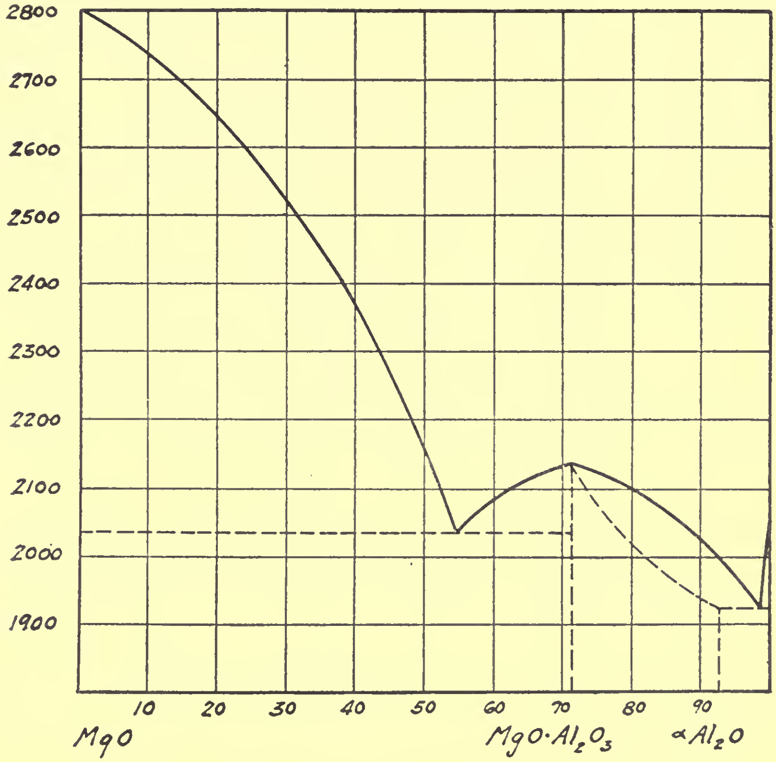

FIG. 2.

presents itself as to the magnitude of the effect of such admixtures upon the refractory power of the magnesia. The answer to this question can be obtained from the phase-rule diagram. The curve in figure 2 shows that if any quantity of alumina, no matter how small and not exceeding 70%, be mixed with the magnesia, the liquefaction temperature, that is the temperature at which liquefaction will *begin*, drops at once from 2800° to 2030°. In other words, alumina, present as an impurity or added for bonding purposes to magnesia, always decreases the initial liquefaction temperature by 770°.

This initial liquefaction temperature is known as the "eutectic temperature," and the first portions of liquid which appear when this temperature is reached will not have the composition of the original body, but instead will have what is known as the eutectic composition, that is, the composition corresponding to the eutectic point, which for the case under consideration is shown by the diagram to be 55% of alumina and 45% of magnesia. The maximum amount of this liquid which can be formed by heating the refractory body to any given temperature can also be readily calculated from the diagram. The resultant weakening of the mechanical strength of the refractory body depends of course upon the amount of this liquid which is formed. A small quantity of liquid might be held in the pores of the body without decreasing very greatly its mechanical strength, but as the amount of the liquid increases the strength of the body continually decreases until finally a cone made of the material is no longer able to stand up under its own weight, owing to the fluidity produced by the presence of the eutectic liquid in its pores.

Turning now to alumina, we notice from the diagram that a refractory body made of pure alumina will show no liquefaction whatever until a temperature of 2050° is reached, while the admixture of any quantity of magnesia not exceeding 30% by weight with the alumina will give a body which begins to liquefy at 1925°, which is the eutectic point on the right of the diagram. It is evident that alumina as an impurity in magnesia produces a much greater lowering in the initial liquefaction temperature than does magnesia as an impurity in alumina.

Whenever a phase-rule diagram exhibits a maximum point, it always means that a chemical compound is formed between the two components, the melting point of this compound being the temperature corresponding to the maximum point and the composition of the compound being the abscissa of this point. Thus the diagram in figure 2 tells us that a chemical compound between magnesia and alumina containing 28% of magnesia and 72% of alumina and hence having the formula $Al_2O_3.MgO$ is formed and that this compound has a melting point of 2135°. If therefore we proceed to manufacture a refractory body by mixing together alumina and magnesia in the molal ratio 1 to 1 (i.e., 28% MgO and 72% Al_2O_3 by weight), we can obtain a product which can be employed as a refractory at any temperature up to 2135° without the occurrence of any liquefaction. This magnesium aluminate is thus a somewhat better refractory than alumina alone, since it will stand a temperature 85° higher than pure alumina will. The diagram also shows that small errors in the composition of the body would not produce very

serious results upon its refractory power since an excess of alumina lowers the liquefaction temperature only 210° and an excess of magnesia only 105°.

In addition to the increase in refractory power which can be obtained by adding to alumina enough magnesia to combine completely with it, certain other advantages are secured at the same time. We have mentioned above the difficulty of securing a bond when manufacturing a refractory out of a single material; in fact, to manufacture a refractory of high mechanical strength out of pure alumina would require either long firing or a firing temperature close to the melting point, that is, a firing temperature of about 2000° which is scarcely practicable on an industrial scale, except with the aid of an electric furnace. By mixing together magnesia and alumina in the molal ratio of 1 to 1 and firing the resultant body, the compound, magnesium aluminate, will form, even at temperatures considerably below its melting point. The formation of this compound, which probably occurs through the gaseous phase owing to the mutual vaporization of the constituents in the pores of the body, usually results in a mass of small interlacing crystals and consequently gives a product of increased mechanical strength and toughness. The formation of this compound is accompanied by a large shrinkage during burning, and a consequent increase in density thus making it desirable to pre-calcine and grind part of the body mixture before shaping into the desired form.

The formation of such a compound between the two materials may also be expected to decrease greatly the volatility of both materials; to increase their resistance toward many chemical agencies and in some cases toward mechanical abrasion.

Still greater mechanical strength, as well as a diminished porosity and greater resistance toward mechanical abrasion than that which is produced by the chemical combination referred to above, can of course be secured by adding to the body a material for the purpose of producing vitrification; but the increased strength and resistance obtained in this way can usually be secured only with the sacrifice of some of the refractory power. While it is not necessarily impossible to produce vitrification without loss of refractory power, extremely high firing temperatures would usually be required to obtain such a result.

The above conclusions may be summed up as follows: Any refractory body manufactured from alumina and magnesia will begin to liquefy at 1925° if it contains less than 71% of alumina, and at 2030° if it contains more than 71% of alumina. But a body having exactly the composition,

71% alumina, will show no liquefaction whatever until a temperature of 2135° is reached. The amount and composition of the liquid which is formed by heating a body composed of magnesia and alumina in *any given* proportions to *any given* temperature can be exactly calculated from the phase-rule diagram. Owing to the formation of a chemical compound between the constituents, decreased volatility with increased mechanical strength and resistance to abrasion and chemical action may be looked for. Numerous other examples illustrating the value of phase-rule diagrams in solving problems connected with the preparation and behavior of refractory materials might be cited.[5]

Among the substances which might properly be included in a comprehensive phase-rule investigation of refractory materials are the following: carbon, silica; the oxides of calcium, strontium, barium, magnesium, and beryllium; the oxides of alumina, iron, chromium and molybdenum; the oxides of titanium and zirconium; various rare earth oxides; and certain nitrides and carbides—such as boron nitride and silicon carbide. In addition to these substances, the oxides of the alkali metals should also be included because of their common occurrence as impurities in refractory raw materials and their powerful fluxing action, made use of in producing vitrification.

The total number of different systems which could be prepared by the combination of even 20 different components, up to and including four-component systems, is at least 6195, so that evidently the task of making anything like an exhaustive investigation covering all of the above materials would be enormous. It is evident therefore that a selection of the systems to be studied would be necessary, based upon the relative importance of these systems for practical purposes.

Most of the experimental work which has been required in order to complete the study of the few systems which have thus far been thoroughly investigated has been carried out in the Geophysical Laboratory of the Carnegie Institution of Washington. The phase-rule diagrams for the following systems have thus far been wholly or partially completed:

1. One-component systems: silica, alumina, magnesia, lime, carbon.

2. Two-component systems: silica-alumina, silica-magnesia, silica-lime, ferric oxide-lime, alumina-lime, alumina-magnesia, hematite-magnetite.

3. Three-component systems: silica-alumina-magnesia, silica-alumina-lime, silica-magnesia-lime, alumina-magnesia-lime.

4. Four-component systems (partial studies only): silica-alumina-magnesia-lime, silica-alumina-lime-soda, silica-alumina-potash-soda.

5. Five-component systems (partial studies only): silica-alumina-magnesia-lime-soda.

In view of the special knowledge and experience which the Geophysical Laboratory has obtained in dealing with the difficult problems connected with phase-rule investigations at high temperatures, it would certainly be advantageous if the direction and control of the work of a Division of Phase-Rule Investigations could be centered at this laboratory. In order to do this satisfactorily, it would probably be best to establish, if possible, a section in that laboratory for the special purpose of planning and conducting phase-rule investigations from the standpoint of the importance of these investigations to the subject of refractory materials. The work of the present staff of that laboratory is naturally inspired by geological interests and the phase-rule diagrams which have been worked out there are the result of the importance of these diagrams in their bearing upon geological and mineralogical problems rather than of their importance in relation to refractory materials.

In addition to the actual experimental work which might be carried out at the Geophysical Laboratory in accordance with some coöperative arrangement, an advisory supervision and coördination of investigations along similar lines in other laboratories could to advantage be centered in the same institution which would thus become the headquarters for this Division.

In case the necessary arrangements could not be made with the Geophysical Laboratory, it would then be best, if possible, to center the work of this Division at one of the other institutions having well equipped ceramic laboratories. The Bureau of Standards, the Bureau of Mines, the ceramic departments of several of the universities, and perhaps of certain private institutions should receive consideration in this connection.

10. Division 3. Physical constants.—It would be the duty of this Division to compile all the available data concerning the physical, chemical and ceramic properties of refractory raw materials and manufactured products, to keep this compilation up-to-date in a readily accessible form, to promote the necessary investigations for increasing our knowledge of such properties, and to secure the coöperation of all investigators in this field to the end that experimental methods might be improved and standardized, and undesirable duplication avoided. Eventually this Division might desire to establish a laboratory of its own or arrange to have its work carried out by special arrangements with some existing laboratory, such for example as the Bureau of Standards.

11. *Division 4. Standard methods for testing refractory products.*—The function of this Division would be the development of standard methods for testing products in order that the results of such tests should indicate as clearly as possible the behavior which might be expected of each material under service conditions. The methods to be employed in testing a given material would naturally vary according to the use to which the material was to be put. The work of this Division should be correlated with that of the American Society for Testing Materials and the corresponding committees of the American Ceramic Society. For a time at least, the experimental investigations might be carried out by enlisting the coöperation of a number of different laboratories and the work might to advantage be centered at the Bureau of Standards.

The work of Divisions 3 and 4 deals with questions which are probably the most pressing ones at the present time. That is, an accurate and complete knowledge of the properties of refractory materials and products and the development of tests which will accurately depict the behavior of these materials under service conditions are very much needed.

12. *Division 5. Raw materials specifications.*—This Division would formulate the specifications to be met by each raw material employed in the manufacture of each type of refractory product. These specifications would cover such factors as chemical and mineralogical composition, crystallographic condition, texture, state of mechanical division, fusibility, and all the important ceramic properties such as plasticity, burning behavior, properties developed on burning, etc. The work of this Division might also be carried on for a time and perhaps permanently by coöperative arrangements with existing laboratories.

13. *Division 6. Manufacturing methods.*—This Division would study the processes employed in manufacturing each type of refractory and recommend such changes as would result in improvements in quality, decreased cost of production and increased definition and standardization of product. Every effort should be made to design and manufacture refractories adapted to the special requirements of the furnace in which they are to be used. That is, insofar as commercially practicable, the refractory should in each instance be made for the furnace, not the furnace for the refractory. In an actual working organization, it would perhaps be desirable to unite divisions 5 and 6.

14. *Division 7. Standard Specifications for Refractory Products.*—This Division, as well as Divisions 4 and 6 above, should probably be organized in sections, with a section for each industry requiring a special class of refractories. Among the most important users of refractory products which would be represented by sections in this Division, are:

1. The iron and steel industry.
2. The various non-ferrous metal industries.
3. The gas industry.
4. The by-product coke industries.
5. The glass industry.
6. The pottery and porcelain industries.
7. The brick, tile and sewer pipe industries.
8. The cement industry.
9. The various industries employing electric furnaces.
10. The enameling industries.
11. The great variety of chemical industries employing high temperatures.
12. Power plants.

Each section would draw up the specifications which should be met by each type of refractory required in the corresponding industry.

The labors of this Division should be closely correlated with those of Divisions 3, 4 and 6, the work of which would, to a large degree, constitute the foundations upon which this Division would build. In a working organization, it would perhaps be desirable to unite Divisions 4 and 7.

15. Division 8. The engineering division.—The principal work of this Division would be in connection with the design and methods of operation of industrial kilns and furnaces, the purpose being to establish the best design of furnace or kiln and the most efficient method of operating the same for each particular industry or process employing high temperatures. This Division would perhaps be organized in sections corresponding to the various types of furnaces required. Owing to the large scale experiments involved in research in this field, it is clear that large expenditures would be required for carrying out any extensive research program.

16. Division 9. Geology and mining.—The function of this Division would be to promote the extension of geological surveys looking toward the location and mapping of deposits of refractory raw materials, to investigate any other geological problems of importance to the subject, and to secure the further study and development and greater utilization of improved methods of mining, handling and preparing these materials. This Division should coöperate with the United States Geological Survey, the United States Bureau of Mines, the Association of American State Geologists, and the National Research Council, which organizations have recently formulated and are putting into effect a plan for a coöperative survey of the ceramic resources of the country. A descrip-

tion of this plan is contained in the proceedings of the Pittsburgh Conference.[6] This Division would coöperate closely with Division 5.

17. Division 10. Coördination and international coöperation.—This Division would be composed of the chiefs of each of the other Divisions together with representatives of the National Research Council, and possibly of other organizations, under the presidency of the Scientific Director. It would be the duty of this Division to see that the necessary coördination was secured in the labors of each of the other Divisions and to promote any desirable international coöperation in refractory materials research. The headquarters of this Division might advantageously be located at Washington, and as far as international relations are concerned, the work of the Division could perhaps be most conveniently transacted through the international connections already established by the National Research Council.

This Division might also prepare a research census of all agencies engaged in refractories research and arrange to receive regular reports of progress.

An attempt to form an organization for coöperative research in refractory materials has been made in England and a report dealing with (*a*) Refractory materials required by the various industries; (*b*) The laboratory facilities available for refractory research in public institutions of Great Britain and Ireland; (*c*) The facilities existing in England for collecting and publishing information on refractory materials; (*d*) The problems calling for the most important action; and (*e*) The special requirements of each industry, was adopted by a conference held at London, in July, 1917, and has been published. The writer is informed that plans have been perfected for the immediate establishment in England of a research laboratory similar to the Geophysical Laboratory of the Carnegie Institution, for the purpose of conducting investigations of the fundamental chemical and physical properties of refractory materials.

The ceramic industries of France have also recently formed an association known as the *Syndicat des Fabricants de Produits Ceramiques de France* and coöperative relations should be established with the refractories section of this association.

18. Financing the research organization.—An organization constituted in accordance with some such scheme as that outlined in the foregoing pages would require liberal financial provision for its operation. Ample financial resources for inaugurating the undertaking might be secured if each producer of refractory materials or products would contribute to a

common fund an annual self-imposed tax of say 0.2 of 1% of the annual sales value of his output. In comparison with the tax which his business pays to state and nation, to fire, risk, and liability companies in the form of insurance premiums, and to legal counsel in the form of retaining fees, a research tax of 0.2 of 1% is insignificant. Such a tax would provide an annual income of over $100,000 for a Refractories Research Corporation, and this income would automatically increase from year to year with the growth of the industry. If users of refractories, as well as producers, were admitted to the organization (and this would be highly desirable) the above estimated annual income of the Research Corporation could be increased by more than 50%, by a similar rate of taxation on the annual purchase value of all refractories purchased by each user.

In this connection the following paragraphs from a recent address delivered by Dr. John Johnston before the American Zinc Institute are much to the point:

Most large firms take out insurance of various kinds and make regular allowance for depreciation of plant and equipment; comparatively few make expenditures on research as a fixed charge on their business. And yet this insurance against ignorance is comparatively cheap; one large firm considers it certain that the amount gained directly from their research work—without taking into accouut the less tangible, though certain, benefits—has been *at least* ten times its cost. But to get the full benefit of such insurance it is necessary to go systematically into the fundamentals of the question, to ascertain precisely what is happening at each stage of the operation. The absolute necessity of such fundamental work is insisted upon by all of the big firms which have gone into systematic research work and found it profitable. This implies a fairly large expenditure which, though a relatively small matter for a large firm, would not be possible to a small firm because it would constitute too large a charge on its total annual product. But smaller units may organize to carry out research work coöperatively, and so gain equal, if not greater advantage at a comparatively small cost to each individual unit.

The National Canners Association some years ago established in Washington a laboratory to take up some of the difficulties of the canning industry; and this laboratory has been so successful that it is now considered to be one of the assets of the industry. In Britain the plan of establishing a coöperative research organization is being considered by a number of industries; the most substantial progress has been made by the cotton industry, a provisional committee of which has worked out a scheme of procedure in considerable detail. They are establishing the British Cotton Research Association that will include as members, cotton-spinning and thread-making firms, manufacturers of cloth, lace and hosiery, bleachers, dyers, printers and finishers; it will conduct researches which include the study of the cotton plant at one end and the 'fin-

ishing' of the manufactured article at the other, and also encourage and improve the education of persons who are, or may be engaged in the industry. They have published a very interesting pamphlet* on 'Scientific Research in Relation to Cotton and the Cotton Industry,' in which a popular account of the matter is given. It would lead too far to go into the matter but this report brings out one important point deserving of mention here—namely, with respect to the cost of such research work to each member of the Association. On the basis that the Association would spend $250,000 a year on research work, it is shown that the cost to each member would be only about 10% of his fire insurance premium, 25% of the cost of health insurance, or about 20% of the cost of employers' liability insurance. In other words, the scientific and technical health of the industry can be insured at a very small cost.

The organization of most of the Divisions would naturally be a gradual process dependent in each instance upon the finding of the right man to head the Division and the working out of a definite research program which would receive the approval of the Board of Trustees. Any attempt to create from the beginning a full fledged organization, such as that outlined above, would probably result in numerous disappointments. A not improbable eventual development of the work might be the establishment of a large central laboratory and testing station in which all of the research work of the Association would be carried out. The experience of several of the large corporations, such as the General Electric Company and the Eastman Kodak Company, and of the National Canners Association, has demonstrated the success of this method of conducting industrial research. Some of the obvious advantages of this concentrated form of organization over the distributed type of organization are (1) the opportunity for frequent personal conferences among the different types of experts on the staff; (2) the avoidance of duplication of equipment; (3) the saving of the time and energy of the Director. The first of these is probably the greatest virtue of the concentrated form of organization and is the one to which its great success is most largely due.

19. The practicability of forming a refractories research corporation.—Whether and in how far it is feasible, under the industrial and economic conditions which exist in the refractories industries at the present time, to form a research corporation for the purpose of prosecuting coöperative research in this field could probably only finally be determined by attempting to form such an organization. Viewed purely from the scientific side, the field is a sufficiently homogeneous one to make such an

* Copies obtainable from the Secretary, 108 Deansgate, Manchester; (price nine pence).

organization practicable and desirable, but viewed from the industrial and commercial side, this can hardly be said to be the case. The manufacturers themselves and many of the users of refractory materials are industrial competitors and this element of competition is alone sufficient to make the actual realization of any such plan as that proposed here extremely difficult, if not quite impossible. Industrially and commercially the field is a very heterogeneous one, involving many diverse and conflicting interests. Some of the larger manufacturers already have their own research laboratories for dealing with the problems peculiar to their own product, and the first interest of each manufacturer is naturally the well being of his own business rather than the development and perfection of our knowledge of refractory materials in general.

The preparation of any research budget to be defrayed by appropriations from a common fund contributed to by *all* manufacturers and users of refractories would present almost insuperable difficulties. Perhaps the only Divisions in which anything like unanimous agreement as to expenditures could be secured would be Divisions 1 and 9. In the case of the other Divisions it would seem that a budget could be agreed upon only if the expenses of the different undertakings in each Division were defrayed by those manufacturers and users to whom the results of these particular investigations would be of direct and immediate value. For example, to take an extreme case, one could hardly expect that the manufacturers of clay refractories would be especially interested in helping to defray the expenses of an investigation of boron nitride as a refractory. Certainly if any part of a common fund were used in this way, any contribution of the manufacturers of clay refractories towards such investigations would be a purely altruistic one. Furthermore, any common fund created by contributions based upon the sales and purchase value of products would in large part be made up of contributions from manufacturers and users of a comparatively small number of types of refractories, since most of the tonnage of refractories used in modern industry consists of clay and silica materials, and these contributors would naturally be primarily interested only in investigations dealing with these particular classes of refractories. For the same reasons any considerable expenditure for the work of Division 2, for example, could hardly be expected from other than altruistic motives, since the phase-rule diagrams for the refractory materials most largely used and for which the necessary tonnage of raw materials is in sight have already been worked out and hence the development of any refractory which would to any considerable degree replace any of these materials would only

be commercially possible in case it had a much longer life under service conditions than the types of refractories now employed.

Moreover, it could hardly be expected that the manufacturers of a given type of refractory would be interested in promoting an investigation which might conceivably result in the perfection of a product of sufficient commercial practicability to destroy or to greatly injure their own business, however desirable from a national viewpoint such a result might be. Certainly such investigations could be undertaken only if adequate provisions for safe-guarding the financial interests of all members against such possibilities as the above could be worked out. A single industrial corporation, such for example as the General Electric Company, can undertake investigations leading to the development of products which may require the scrapping of manufacturing facilities representing large investments, but for an association of more or less competitive interests to undertake any such investigations on a coöperative basis has obviously great difficulties, especially if both manufacturers and users are included in the organization. These difficulties would, it is true, be greatly diminished if the association included only users of refractory materials, and for this reason it may be that the country will eventually have to look to the consumers of refractories for the prosecution in a large way of systematic research in this field.

It seems clear to the writer that any such organization as the 'ideal' one presented in the preceding pages could scarcely be developed even eventually except by private or governmental endowment or by the actual industrial amalgamation of all or the greater part of the refractories interests of the country. In view of these facts it may be that the above survey of the scientific aspects of the subject has no practical value at the present time, but if it serves only to promote discussion, to arouse further interest in research in this field, and to bring about any further degree of coöperation, its purpose will be fulfilled. Some type of organization for accomplishing at least a portion of the work outlined above ought to be feasible. Perhaps several more or less independent organizations, instead of one, would be required, or perhaps an association of research laboratories engaged in refractories research might be able to perfect some practicable scheme of coöperation. Certainly, viewed solely from a national economic viewpoint, the stimulation of research in this field is greatly needed, and in addition to supporting the investigation of those problems which seem most urgent from the 'practical' viewpoint, it is to be hoped that to some degree at least manufacturers and users of refractories will be willing to make some contributions from

more purely altruistic motives; that is, that they will feel ready to take some share in the promotion of all classes of investigations in their field, even though they see no possibility of direct or immediate financial return to themselves. Such contribution might take the form of direct financial assistance or the form of supporting the efforts of federal, state and endowed institutions to secure larger appropriations for carrying out some of the more fundamental scientific work, even though some of this work may seem to be largely of the type ordinarily classed as 'pure science,' and perhaps appear to be more or less visionary or 'impractical.' Certainly the history of the development of science and industry has repeatedly demonstrated the enormous ultimate value of research work of this character.

[1] See also Geo. A. Balz, Why Refractories Are a World Necessity, *Brick and Clay Record* 48, 741 (1916).

[2] "It will be recognized by all who have studied the matter closely that the future industrial success of any country will largely depend upon the extent to which it develops high temperature processes." Cantor Lecture, by C. R. Darling, before the Royal Society of Arts, London, February, 1918.

[3] For a statement of the factors which determine the fusibility of a material, see Washburn, *Trans. Am. Ceram. Soc.*, 19, 195 (1917).

[4] See Rankin and Merwin, *J. Am. Chem. Soc.*, 38, 571 (1916).

[5] See Sosman, *J. Ind. Eng. Chem.*. 8, 985 (1916); *Trans. Far. Soc.*, 12 (1917).

[6] *The Clayworker*, 69, 759 (1918).

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